

Possible superconductivity above 400 K in carbon-based multiwall nanotubes

Guo-meng Zhao* and Y. S. Wang

Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204, USA

Magnetization and resistance measurements were carried out on carbon-based multiwall nanotubes. Both magnetization and resistance data can be consistently explained in terms of bulk superconductivity above 400 K although we cannot completely rule out other possible explanations to the data.

Seven years after the discovery of the 30 K superconductivity in a single-layer copper-based oxide [1], the superconducting transition temperature T_c was raised up to 153 K in a mercury-based three-layer cuprate under a pressure of 17 kbar [2]. Meanwhile, high-temperature superconductivity as high as 40 K was observed in electron-doped C_{60} (see a review article [3]). Last year, the superconductivity at 52 K was observed in hole-doped C_{60} [4]. Very recently, a maximum $T_c = 117$ K has been discovered in a hole-doped $C_{60}/CHBr_3$ [5]. It was also suggested that [5] the maximum T_c might reach up to 150 K if one could expand spacing between the C_{60} molecules further. Here we report magnetization and resistance measurements on carbon-based multiwall nanotubes. Both magnetization and resistance data can be consistently explained in terms of bulk superconductivity above 400 K although we cannot completely rule out other possible explanations to the data.

The commercially available multiwall nanotubes were prepared from the high-purity graphite (99.9995%) by an arc process with no metal catalysts. The nanotubes consist of 5-20 graphite layers with 2-20 nm in diameter and 100 nm to 2 μ m in length. The tubes are normally assembled into a bundle, and the bundles are assembled into ropes. We selected several ropes with a diameter of 0.05-0.1 mm and a length of 0.5-1 mm for resistivity measurements. The four point contacts were attached by conductive silver epoxy and the contact resistance is in the range of 20-60 Ω . Magnetization was measured by a quantum design superconducting quantum interference device (SQUID). We can attain high accuracy in the measurements by using the reciprocating sample option (the accuracy is better than 3×10^{-8} emu). The SQUID response is well centered at each temperature. The “zero-field” of less than 3 mG was achieved by using the ultra-low field option. The magnitude and direction of an applied magnetic field were determined by comparing the diamagnetic signal of a standard Pb superconductor.

In Fig. 1a, we show temperature dependence of the field-cooled (FC) susceptibility in the magnetic fields of 20 mG and 280 mG for sample ZWC, which has a weight of 165 mg. The sample was cooled in the fields from

400 K. The sample did not experience any high magnetic fields before these measurements. It is apparent that the diamagnetic susceptibility persists up to 400 K; the diamagnetic signal at 5 K corresponds to about 0.2% of the full Meissner effect. It is remarkable that the diamagnetic susceptibility strongly depends on the magnetic field. Moreover, there is a kink feature at $\simeq 110$ K, which may be related to the intergrain Josephson coupling as discussed below.

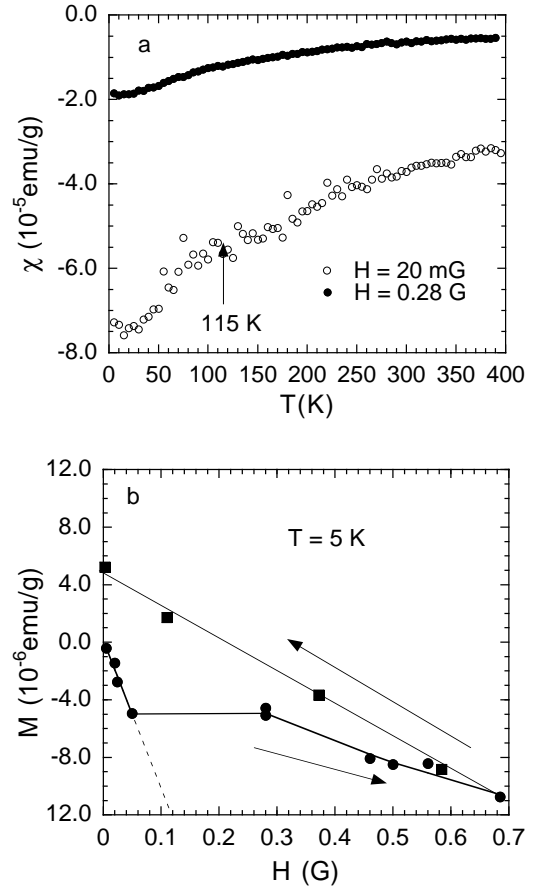


FIG. 1. a) Temperature dependence of the field-cooled (FC) susceptibility for sample ZWC (168 mg) in the magnetic fields of 20 mG and 280 mG. b) The FC magnetization as a function of field in the low-field range.

The strong field dependence of the diamagnetic susceptibility cannot arise from the core diamagnetism of the carbon ions and/or from the orbital diamagnetism of conduction electrons. In addition, the moment of our sample holder is linearly proportional to the field and has a magnitude of -1.9×10^{-5} emu in the field of 0.1 T. The observed strong field dependence of the diamagnetic susceptibility in this material is similar to that in single crystalline and polycrystalline samples of the cuprate superconductors [6,7].

In Fig. 1b, we display magnetization as a function of the field in the low field range. In the very low field range, the magnetization is linearly proportional to the field, as expected for a superconductor. Furthermore, the detailed field dependence of the magnetization at 4.2 K from the earth field to 10 T was reported in Ref. [8]. The field dependence of the magnetization in the low field range (Fig. 1b) and in the high field range [8] is similar to that for a heavily overdoped $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+y}$ in a temperature slightly below T_c (~ 15 K) [9]. A possible theoretical explanation to the unusual field dependence of the magnetization can be found in Ref. [10].

Fig. 2 shows the field-cooled and zero-field cooled (ZFC) susceptibility. For the ZFC measurement, the sample was cooled from 400 K to 5 K in a field of less than 3 mG, and then a field of 280 mG was set. After the measurement was finished, the field was precisely determined by comparing the diamagnetic signal of a standard Pb superconductor. It is clear that the difference between the ZFC and FC signals is significant (about 15 % of the FC signal at 5 K). This behavior is also expected from a superconductor, as seen in cuprates where the difference between the ZFC and FC signals is about 20-30% of the FC signal [6].

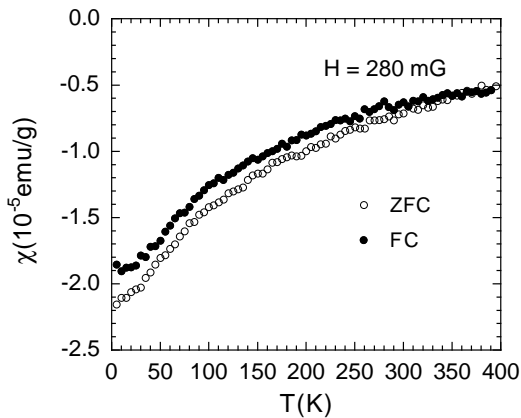


FIG. 2. Temperature dependence of field-cooled and zero-field cooled (ZFC) susceptibility. It is clear that the difference between the ZFC and FC signals is significant (about 15% of the FC signal at 5 K).

Fig. 3 plots the remnant magnetization as a function of temperature. A magnetic field of 5 T was applied at 400 K. After the sample was cooled from 400 K to 5 K under the field, we set the field to zero (the real field is -1.1 G) and measured the magnetization from 5 K to 400 K. One can clearly see that the temperature dependence of the M_r is similar to that of the diamagnetic susceptibility in a field of 20 mG except for the opposite signs (see Fig. 1a and Fig. 3). This behavior is expected for a superconductor, as seen in cuprates [6]. If there were a mixture of a ferromagnet and a material with field independent diamagnetic susceptibility, the total susceptibility would tend to turn up below 120 K where the M_r increases suddenly. In contrast, the low-field susceptibility suddenly turns down rather than turns up below 120 K. This provides strong evidence that the observed M_r in the nanotubes is intrinsic and has nothing to do with the presence of ferromagnetic impurities. In addition, by comparing the magnitude of the M_r for the present sample with that for the sample in Ref. [8], one can see that the remnant moment M_r is nearly proportional to the magnitude of the diamagnetic susceptibility. This gives further support to the explanation that the M_r is related to the diamagnetism rather than to the presence of ferromagnetic impurities. The fact that the M_r remains up to 400 K implies that the bulk superconductivity might persist up to 400 K.

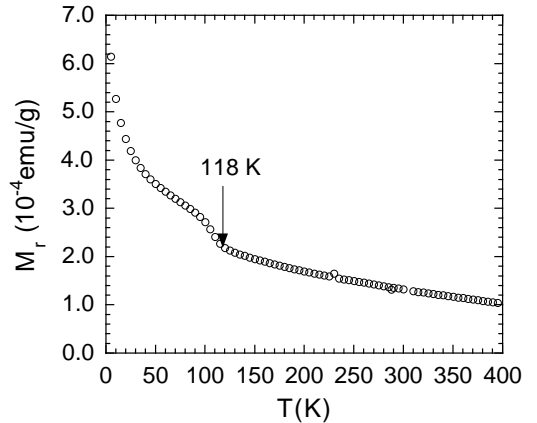


FIG. 3. The remnant magnetization as a function of temperature for sample ZWC. A magnetic field of 5 T was applied at 400 K. After the sample was cooled from 400 K to 5 K under the field, the field was set to zero and the magnetization was measured from 5 K to 400 K.

It is known that the magnitude of M_r in a superconductor is proportional to the critical current density J_c . The fact that the magnitude of M_r is rather small and decreases rapidly with increasing temperature suggests that the critical current is limited by intergrain Josephson

coupling. There is a pronounced kink feature at $\simeq 120$ K in the diamagnetic susceptibility curve (see Fig. 1a), and in the M_r curve (see Fig. 3a). This feature may be related to the Josephson coupling among the bundles. There may be a stronger intertube Josephson coupling within the bundles, which may persist up to 400 K in the very low fields. This can naturally explain why the low-field (20 mG) susceptibility is substantially higher than the “high-field” (> 0.28 G) susceptibility for $T < 400$ K. It appears that a field of > 0.28 G is strong enough to suppress the Josephson coupling.

In Fig. 4a, we present the resistance data from 300 K to 750 K for sample ZW-8. The sample was measured in flowing Ar gas to avoid oxidation. The solid black line is the fitted smooth curve below 550 K. It is remarkable that the resistance suddenly turns up above 600 K, which may manifest the resistive transition to the normal state within the individual superconducting tubes although we cannot completely rule out other possibilities. Such a temperature dependence of the resistance is reproducible in all the three samples in warming up measurements. However, the resistance becomes lower and the resistance jump nearly disappears for the cooling down measurements. This could be understood as follows. If T_c is widely distributed, the resistive path could be shortened by a superconducting path with higher T_c for cooling down measurements (i.e., the current path is possibly altered for the cooling down and warming up measurements).

The non-zero resistance below T_c might be due to the fact that the superconducting fraction f_s in the ropes is not large enough to reach a percolation limit. Another possible reason is that the transport has 1-dimensional nature, so that the possibility for the short tubes (the average length is about $1\ \mu\text{m}$) to be connected into “long” tubes of about 1 mm (through Josephson coupling) is extremely low. This has been indeed demonstrated in the transport measurements on the ropes of single-wall nanotubes, which show that there exists only one “long” tube in a rope [11]. In worse cases, the intrinsic metallic conductivity in nanotube ropes can be completely masked by the intertube contact resistance and the resistance contributed from semiconductive tubes. The semiconducting behavior of the rope will still remain when some individual short tubes become superconducting. Even if there possibly exist several “long” tubes, the current density within the small number of the “long” tubes may exceed the Josephson critical current. Only in one of 14 ropes we measured, we found that the resistance at 5 K decreases with current when the measuring current is less than 10 nA. However, the result could not be reproduced for the second measurement on the same rope possibly because the very weak link was already broken.

In order to see more clearly the resistive transition, we

plot in Fig. 4b the difference $R(T) - R_{fit}(T)$, where

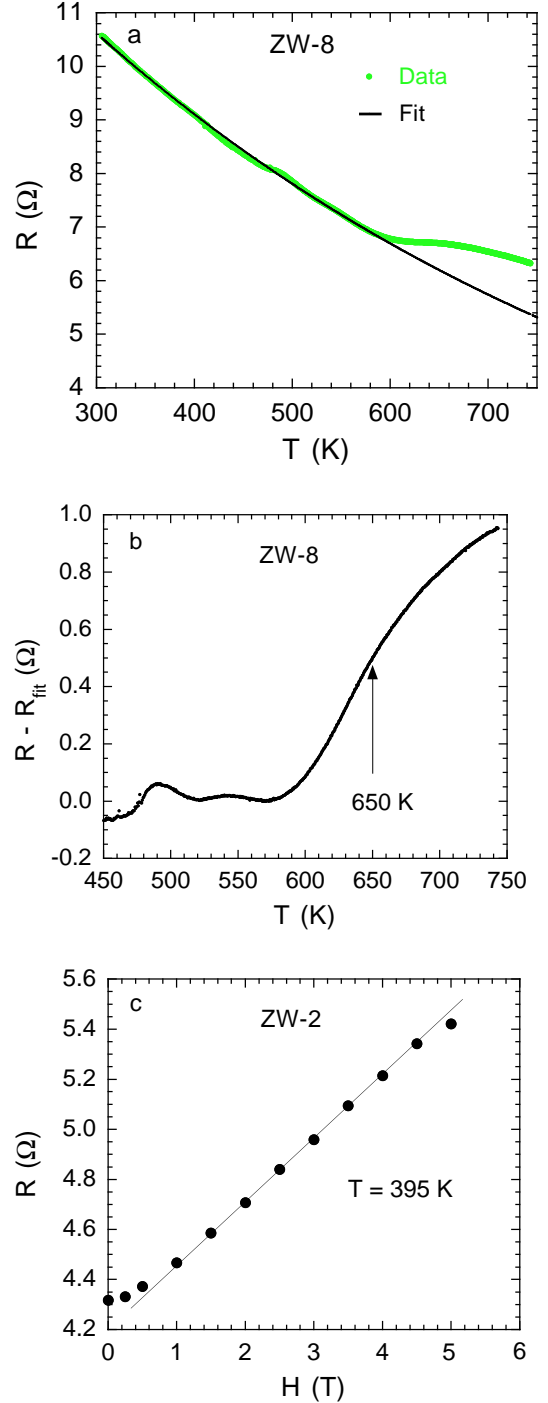


FIG. 4. a) The resistance data from 300 K to 750 K for sample ZW-8. The sample was measured in flowing Ar gas to avoid oxidation. The solid black line is the fitted smooth curve below 550 K. b) The difference between $R(T)$ and $R_{fit}(T)$ ($R_{fit}(T)$ is the fitted black line in Fig. 3a). c) The magnetoresistance (MR) effect for sample ZW-2 at 395 K.

$R_{fit}(T)$ is the fitted curve in Fig. 4a. The transition appears rather broad and may be incomplete even at 750 K. The resistance jump at T_c is on the order of $1\ \Omega$. This is in good agreement with the magnetoresistance effect at 395 K, as shown in Fig. 4c. The resistance was measured when the field was applied perpendicular to the axis of the rope. It is clear that there is a large positive magnetoresistance (MR) effect for the field between 0.5 T and 4.5 T. For the field below 0.5 T and above 4.5 T, the MR effect appears saturated. This behavior is also expected from a superconductor (for an example, see Fig. 5 of Ref. [12]). It is striking that the resistance jump from the superconducting to the normal state is also on the order of $1\ \Omega$, in agreement with the result shown in Fig. 4b. This consistency implies that the resistance jump at about 650 K should be related to the superconducting transition. Then the normal state resistivity should be on the order of $1000\ \mu\Omega\text{cm}$. Considering the correction for the porosity of the ropes [13], the normal state resistivity of the superconducting tubes would be on the order of $20\ \mu\Omega\text{cm}$, which is comparable with that ($\sim 34\ \mu\Omega\text{cm}$) for the metallic single-wall nanotubes [14].

Now we turn to discussion of the Meissner effect. For decoupled superconducting grains, the diamagnetic susceptibility is given by [10]

$$\chi(T) = -f_s \frac{\bar{R}^2}{40\pi\lambda^2(T)}, \quad (1)$$

where \bar{R} is the average radius of spherical grains and $\lambda(T)$ is the grain penetration depth, which must be larger than \bar{R} in order for Eq. 1 to be valid. In the present case, the grains are not spherical but cylindric. We may replace \bar{R} by \bar{r} , and $1/40$ by $1/60$ (due to a difference in the demagnetization factor) when the measuring field is along the tube axis direction, where \bar{r} is the average radius of the tubes. With $\bar{r} = 50\ \text{\AA}$ [15], $f_s = 0.15$, weight density of $2.17\ \text{g/cm}^3$ [16], and $\chi_{||}(0) = -1.1 \times 10^{-5}\ \text{emu/g}$ [15] (we have ignored the diamagnetic contribution in the normal state, which should be about $-5 \times 10^{-7}\ \text{emu/g}$ according to a simple rolling model of graphite sheets), we find that $\lambda_{||}(0)/\bar{r} = 5.8$, and $\lambda_{||}(0) \simeq 289\ \text{\AA}$. If we assume $f_s = 1$, then $\lambda_{||}(0) \simeq 746\ \text{\AA}$, which is also quite reasonable. Now if we take $\lambda_{||}(0) \simeq 1600\ \text{\AA}$ (close to that for optimally doped cuprates), and $f_s = 1$, we calculate $\chi_{||}(0) = -2.4 \times 10^{-6}\ \text{emu/g}$. Therefore, even if there is bulk superconductivity, the Meissner effect could be negligible because $\lambda_{||}(0)/\bar{r} \gg 1$. Only if the tubes are Josephson coupled in very low magnetic fields, the Meissner effect can be substantial.

It is known that the resistance of a superconducting wire measured through normal Ohmic contacts (two probe method) is not negligible because the number of the conductance channels in the wire is much smaller

than in the contacts, as shown recently by Kociak *et al.* [17]. Kociak *et al.* [17] observed superconductivity at 0.55 K in single-wall carbon nanotube bundles; the resistance drops by two orders of magnitude below 0.55 K. Below T_c , a finite resistance of $74\ \Omega$ is observed for a bundle consisting of 350 tubes in parallel (the contact resistance is very small). This implies that the resistance of each tube below T_c is equal to $74 \times 350 = 25.9\ \text{k}\Omega \simeq 2R_Q$ (where $R_Q = h/2e^2 = 12.9\ \text{k}\Omega$). There have been no reports that this quantum resistance is observed in the normal state of any metallic single-wall nanotube with a length of $1\ \mu\text{m}$ although a resistance of $R_Q/2$ is predicted for a normal metallic single-wall nanotube [18] assuming ballistic transport. To ensure ballistic transport within a length of $1\ \mu\text{m}$, the mean free path of a nanotube must be larger than $1\ \mu\text{m}$, which is very unlikely at room temperature. The inelastic scattering by a very low optical phonon mode (about 2 meV [19]) should be rather strong at room temperature [20]. Moreover, it was also shown that the linear T dependence of the resistivity in metallic single-wall nanotubes arises from the inelastic scattering by a deformation mode (“twistons”) [21]. These inelastic scatterings would strongly limit the mean free path at room temperature (the mean free path at room temperature can be estimated to be on the order of $100\ \text{\AA}$ from the measured resistivity), and make it impossible for a $1\ \mu\text{m}$ long tube to have ballistic transport at room temperature.

In contrast, the quantum resistance of $2R_Q$ or R_Q was observed for a $4\ \mu\text{m}$ long multiwall nanotube even at room temperature [22]. This was taken as evidence for ballistic transport in this multiwall nanotube [22]. However, there have been no reports that the quantum resistance is observed in the normal state of any metallic single-wall nanotubes. The fact that the quantum resistance is observed only in the superconducting state of a single-wall nanotube [17] implies that the observation of the quantum resistance should be associated with superconductivity in the tube. By analogy, the observation of the quantum resistance at room temperature in the multiwall nanotube [22] implies that the multiwall nanotube is actually a room temperature superconductor. If the superconductivity only occurs in the outer two layers of the tubes, one can naturally explain the observed quantum resistance of $2R_Q$ or R_Q [22]. The resistance of $2R_Q$ corresponds to the case where only one of the superconducting layers is connected to the metal contacts, as in the case of the superconductivity in the single-wall nanotube [17], while the resistance of R_Q corresponds to the case where the two superconducting layers are connected to the metal contacts. Furthermore, the tube does not dissipate heat with current density $> 10^7\ \text{A/cm}^2$ [22]. This is possible only if the tube is a room temperature superconductor or there is no inelastic scattering in the

normal state of the tube. Since the inelastic scattering is inevitable at room temperature [20,21], the nondissipative feature of the tube should be related to the superconductivity. Moreover, superconductivity of about 20 K has been observed in the metallic single-wall nanotubes [23]. Presumably, the pairing mechanism in the single-wall nanotubes should be similar to that in doped C₆₀, which is phonon-mediated [3]. This implies that electrons should be coupled to lattice rather strongly in these nanotube materials so that the inelastic scattering is not very weak.

The much lower superconductivity in single-wall nanotubes than in multiwall nanotubes may be associated with the interlayer coupling strength. For multiwall nanotubes, the interlayer coupling should be much stronger than for the single-wall nanotubes, leading to a much higher T_c . Theoretically, within the phonon-mediated mechanism, it is possible to have high temperature superconductivity in these carbon-based materials due to a very high phonon frequency ($\omega = 2400$ K) [19]. A simple estimate suggests that an electron-phonon coupling constant of about 2 can lead to a T_c of about 460 K. It was also shown that the very low-energy whispering mode can produce a very large pairing potential [20]. Alexandrov and Mott [24] estimated that the highest T_c within a strong electron-phonon coupling model is about $\omega/3$, which is about 800 K.

Although the present data along with the nondissipative feature and the quantum resistance observed for the multiwall nanotubes at room temperature [22] can be well explained by superconductivity above room temperature, we cannot completely rule out the other possible explanations. For example, ring currents around the tube axis could cause a diamagnetism [25]. Within this model, it seems difficult to explain why the diamagnetic signal in 20 mG for the coupled tubes is about one order of magnitude larger than for the physically separated tubes, and why the diamagnetism in the low fields is so strongly dependent on the field. Since the energy scale of the magnetic field is so small compared with any other energy scales, it is hard to imagine that the extreme sensitivity of the diamagnetism to the field could be also understood by the other models. More rigorous theoretical and experimental efforts are required to finally pin down whether the observed phenomena can be only explained by superconductivity. Instead of giving a definite claim for the superconductivity above room temperature in the multiwall nanotubes, we would like the readers to make their own judgment based on the present experimental data.

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Correspondence should be addressed to gmzhao@uh.edu.

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